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Changes in soil water availability in vineyards can be traced by the carbon and nitrogen isotope composition of dried wines

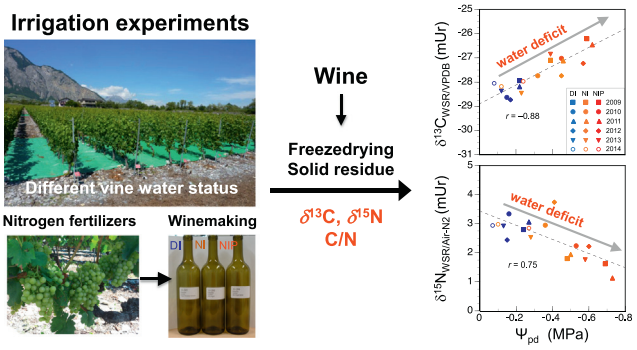
Jorge E. Spangenberg [a,*], Vivian Zufferey [b]

[a] Institute of Earth Surface Dynamics (IDYST), University of Lausanne, CH-1015 Lausanne, Switzerland
[b] Institute of Plant Production Sciences (IPV), Agroscope, CH-1009 Pully, Switzerland

HIGHLIGHTS

- Field experiment simulated soil water restriction in vineyards under climate change.
- ^{13}C and ^{15}N were analyzed in dried wines from diverse vine water status and vintages.
- ^{13}C-enrichment highly correlates with vine water-stress and dryness of vintage summer.
- N content and $\delta^{15}N$ decrease with soil water deficit due to limited nutrient flow.
- Vine in dried soils uses the internal organic N reserves.

GRAPHICAL ABSTRACT



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ABSTRACT

The grapevine is one of the most important edible fruit plants cultivated worldwide, and it is highly sensitive to changes in the soil water content. We studied the total carbon and nitrogen contents and stable isotope compositions (C/N_{WSR}, $\delta^{13}C_{WSR}$ and $\delta^{15}N_{WSR}$ values) of the solid residues obtained by freeze-drying wines produced from two white grapevine cultivars (*Vitis vinifera* L. cv Chasselas and Petite Arvine) field grown under different soil water regimes while maintaining other climatic and ecopedological conditions identical. These experiments simulated the more frequent and extended climate change-induced periods of soil water shortage. The wines were from the 2009–2014 vintages, produced using the same vinification procedure. The plant water status, reflecting soil water availability, was assessed by the predawn leaf water potential (Ψ_{pd}), monitored in the field during the growing seasons. For both wine varieties, the $\delta^{13}C_{WSR}$ values are highly correlated with Ψ_{pd} values and record the soil water availability set by soil water holding capacity, rainfall and irrigation water supply. These relationships were the same as those observed for the carbon isotope composition of fruit sugars (i.e., must sugars) and plant water status. In Chasselas wines, the nitrogen content and $\delta^{15}N_{WSR}$ values decreased with soil water deficit, indicating control of the flux of soil-water soluble nutrients into plants by soil water availability. Such a correlation was not found for Petite Arvine, probably due to different N-metabolism processes in this genetically atypical cultivar. The results presented in this study confirm and generalize what was previously found for red wine (Pinot noir); the carbon isotope composition of wine solid residues is a reliable indicator of the soil and the plant water status and thus can be used to trace back local climatic conditions in the vineyard's region. In most wines (except Petite Arvine) the C/N_{WSR} and $\delta^{15}N_{WSR}$ values are indicators of the origin of the nitrogen supplied to the plant's fruit (grape) that can be used to assess the N dynamics in the soil-water-plant system.

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* Corresponding author.
E-mail address: Jorge.Spangenberg@unil.ch. (J.E. Spangenberg).

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1. Introduction

Agriculture and food security are some of the sectors most affected by climate and environmental change (Schmidhuber and Tubiello, 2007; Lobell et al., 2008; Bonamente et al., 2016). Among all cultivated crops, the grapevine (*Vitis vinifera L.*) emerges as one of the most important worldwide and the most hydro-climatic sensitive and expensive. Since the past decade, this has motivated various studies focusing on the effect of the plant (vine) water status on fruit maturation and grape and wine quality and quantity (Koundouras et al., 2006; Lund and Bohlmann, 2006; van Leeuwen et al., 2009; Bonamente et al., 2016; Pagay et al., 2016; Rayne and Forest, 2016; van Leeuwen and Darriet, 2016). The chemistry and sensory characteristics of the wine, unlike other crop commodities, are mostly determined by the geographical location of the vineyard, with relatively minor input from the viticultural and winemaking practices (Bisson et al., 2002). This geographical link between the quality and typicity of the wine with the location of grape and wine production, originally referred to in French wines by the term *terroir*, is a concept integrating soil (pedology, geology), climate, and topography (Seguin, 1986; Jackson and Lombard, 1993; van Leeuwen et al., 2004). More recent studies have shown that at least for some vine varieties, most of a wine quality — particularly the development of flavors — is closely correlated with the vine water status (van Leeuwen et al., 2009; Reynard et al., 2011; Picard et al., 2017). Accurate quantification of current water stress on plants and their products, the possibility to trace back its evolution in time, and the associated changes in soil water availability, even at a local scale, are of prime importance in areas under rapidly changing climatic conditions.

The vine water status is closely correlated to the stable carbon isotope composition ($\delta^{13}C$ values) of berry sugar (Gaudillère et al., 2002). This is explained by different isotopic fractionations in plants using the same photosynthetic pathway (i.e., the Calvin-Benson cycle for grapevines) for fixation of atmospheric carbon dioxide but with decreased stomatal conductance for low water availability (O'Leary, 1988; Farquhar et al., 1989; Flexa and Medrano, 2002). The newly formed photosynthate (the carbohydrates glucose and pentose) in the photosynthetic leaf cell form sucrose, which is transported in the vascular system (mainly in the phloem by sucrose translocation through phloem tissue), dislocated, partitioned and unloaded in different plant parts to synthesize all the organic compounds (e.g., proteins, carbohydrates, lipids, chlorophyll) in the different plant organs and tissues. In grapevines, part of the sucrose accumulates in the fruits (berries) during ripening, and the part remaining after the biosynthesis of plant organic compounds is stored as starch in the roots for reserve energy to be used for the development of primary leaves in the next growing season (Zapata et al., 2004; Zufferey et al., 2015). Therefore, the $\delta^{13}C$ values of sugars from berries at harvest or separated from the must before fermentation give an integrative measure of the photosynthetic fractionation during berry ripening with some potential contribution from sugars from the previous growing season (vintage). These $\delta^{13}C_{sugar}$ values have the potential to record the water availability in vineyards during grape ripening (Gaudillère et al., 2002). The main carbon-containing compound in wine is ethanol (8 to >15 vol%, 11.2 vol% on average; Sumby et al., 2010), which is produced by fermentation of glucose. A carbon isotope fractionation of 2 mUr is associated with the fermentation of a C_3-derived glucose to ethanol ($\Delta = \delta^{13}C_{glucose} - \delta^{13}C_{ethanol}$; Hobbie and Werner, 2004). Thus, the carbon isotope composition of wine ethanol, and most probably the total organic carbon in bulk wine will reflect that of the must sugars. Recently, Guyon et al. (2015) reported a good correlation between the $\delta^{13}C$ values of bulk wine and vine water status for different cultivars (Merlot, Cabernet Sauvignon and Cabernet Franc) and vintages (1998–2000). Chemical and physical deterioration of wine may occur during storage (Waterhouse and Elias, 2010). In particular, oxidative spoilage reactions in bottled wine will convert a fraction of the ethanol into acetaldehyde, acetic acid, and its acetals (Escudero et al., 2000; Skouroumounis et al., 2005; Bartowsky and Henschke, 2008). These biochemical reactions are most likely to induce an isotopic fractionation. There are also problems with the bottle closure (cork) that may cause evaporative losses of ethanol. These depend on the temperature of storage and will cause a ^{13}C-enrichment in the wine ethanol. Therefore oxidative spoilage reactions and evaporative losses may cause changes in the ethanol $\delta^{13}C$ values, and thus a difference between the original (after winemaking) and that measured in old wine bottles.

The nitrogen in must and wines appears in the form of inorganic compounds, such as ammonia, nitrate and nitrite anions, and organic compounds, such as amines, amides, free amino acids, pyrazines, nitrogen bases, pyrimidines, proteins, peptides, nucleic acids, amino esters, and vitamins (Moreno-Arribas and Polo, 2009; Sumby et al., 2010; Jackson, 2014). Most of the nitrogen-containing compounds are non-volatile and are therefore preserved in solid residue after drying of the wine. It was shown that the volatile compound concentrations in the solid residue are significantly higher when freeze-drying is used, compared to oven drying at 40–60 °C (de Torres et al., 2010). The dehydrated and dealcoholized solid obtained by freeze-drying wine contains trace amounts of residual fermentable carbohydrates or sugars (i.e., glucose and fructose), non-fermentable carbohydrates (i.e., xylose, arabinose, ribose, rhammose), C_6 higher alcohols, esters, carboxylic acids, ketones, terpenes, C_{13} norisoprenoids, phenolic and heterocyclic oxygen compounds (Moreno-Arribas and Polo, 2009; Sumby et al., 2010). The use of combined carbon and nitrogen molar and isotope ratios (C/N, $\delta^{13}C$ and $\delta^{15}N$ values) in grapevine organs and must is very limited. Two recent studies utilized these discrimination techniques for the optimization of nitrogen partitioning in grapevine organs following foliar urea application (Verdenal et al., 2015, 2016). $\delta^{15}N$ values alone (Paolini et al., 2016) or combined with $\delta^{2}H$, $\delta^{13}C$, and $\delta^{18}O$ (Durante et al., 2016) from the soil-grape-wine system were explored as potential markers of the geographic origin of wines made in Modena and Trento, North Italy. One of these studies showed that neither fermentation nor aging affect the $\delta^{15}N$ of grape must (Paolini et al., 2016); thus, the $\delta^{15}N$ of wine solids would be an indicator of the origin of nitrogen used by the vine and supplied to the berries. Recently we have shown that the carbon and nitrogen stable isotope composition of the wine solid residues ($\delta^{13}C_{WSR}$ and $\delta^{15}N_{WSR}$ values) of Pinot noir red wine, obtained from grapes of field-grown grapevines exposed to controlled soil-plant water status during the 2009 to 2014 growing seasons, is highly correlated with the severity of vine water deficit (Spangenberg et al., 2017). Field experiments were performed under the same geomorphological and pedo-climatic conditions, with the soil-plant water status set up by different irrigation treatments as the only variable (Zufferey et al., 2017). This experimental setup simulates the changes in soil water availability due to global climate changes. The Pinot noir plants were grown under natural conditions with no application of fertilizers and/or amendments in the field, nor the addition of nitrogen yeast-nutrients during the winemaking processes (Spangenberg et al., 2017). It was established that the C/N_{WSR} molar ratios combined with the $\delta^{15}N_{WSR}$ values allow to trace the flow of N-nutrients in soil-grapevine-wine systems.

For the production of white wine, it is generally necessary to optimize the yeast assimilable nitrogen requirements in must (or grape juice) to enhance the fermentation activity and avoid the problems associated with sluggish and/or stuck fermentation and optimize the production of volatile organic compounds (Rapp and Versini, 1995; Alexandre and Charpentier, 1998; Bell and Henschke, 2005; Torrea et al., 2011). This is done by increasing the nitrogen content in grapes via nitrogen fertilization of the vine, and if necessary, by the addition of organic or inorganic nitrogen to the grape juice as a yeast nutrient. The aim of the present study was to investigate if the trends observed for Pinot noir red wines are also valid for white wines derived from grapevines that received nitrogen fertilization and did or did not undergo further addition of organic nitrogen as a yeast nutrient during

winemaking. We investigated the changes in $\delta^{13}C_{WSR}$ and $\delta^{15}N_{WSR}$ values in the white wine varieties Chasselas and Petite Arvine for the same consecutive six vintages (2009–2014) and field irrigation experiments (i.e., drip irrigation, no irrigation, and no irrigation with plastic-covered soil) performed for Pinot noir, but with added nitrogen in the vineyard for plant growth.

2. Materials and methods

2.1. Studied vine varieties and experimental site

The studied wines were produced from grapes stemming from irrigation experiments on field-grown grapevine varieties Chasselas and Petite Arvine conducted from 2009 to 2014 in the experimental station at Leytron (46°11′N; 7°12′E, Canton of Valais, Switzerland) of the Swiss Institute of Plant Production Sciences (Agroscope). Chasselas is one of the most widespread white grape varieties in the world; it is grown in Switzerland, France, Germany, Portugal, Hungary, Romania, Australia, New Zealand, and California in the USA (Vouillamoz and Arnold, 2009). Only in Switzerland is Chasselas cultivated on a broad scale for wine production; it is the second most cultivated grape variety after Pinot noir. Chasselas grapes provide a full, dry, and fruity white wine, very popular in Switzerland, where it has several regional synonym names (e.g., it is called Fendant in Canton Valais and Perlan in some districts of Canton Geneva). Chasselas is an early and vigorous vine, noted for its ability to adapt to different soil properties and microclimatic conditions, bringing forth very subtle expressiveness of each *terroir* (Murisier et al., 2004). Petite Arvine is a grape variety considered autochthonous to the canton of Valais in Switzerland, where it is used to produce a typically highly aromatic white wine (Fretz et al., 2005a). The characteristic aroma and flavor of this internationally renowned Valais white wine is comparable to that of Sauvignon blanc, and these are caused by a subtle mix of organic volatiles with an important contribution of volatile thiols (mainly 3-mercaptohexanol) and β-ionone (Fretz et al., 2005a, 2005b).

The experimental station of Agroscope at Leytron is located in an Alpine valley, 525 m above sea level, with a relatively dry climate, generally warm and temperate, considered to be of the Cfb subtype according to the Köppen-Geiger climate classification, with significant amount of rainfall throughout the year (approximately 600 mm). The meteorological station of Leytron is at the site of the experiment. During the experimental years (2009–2014), the monthly mean precipitation rate varied between 0 and 168 mm, with these extremes in February 2012 and December 2011, respectively; the monthly mean temperatures ranged between −2.7 and 21.8 °C, with the extremes in January 2009 and July 2010, respectively (Zufferey et al., 2017). The vintages from 2009 to 2014 cover the typical average weather conditions during grape ripening at Leytron (Valais, Switzerland) and other wine regions worldwide: hot and dry summer in 2009 and 2011, cool and dry summer in 2010 and 2013, hot and relatively dry summer in 2012, and hot and rainy summer in 2014. The site lies on very stony, >2.5 m deep alluvial soils with a water holding capacity of 150 mm (Zufferey et al., 2017). The atmospheric CO_2 concentration was monitored during the experiment and remained constant for the past 10 years at a level of 390 ppm by volume (ppmv) during daylight, with an increase to 400 ppmv during darkness hours due to plant and soil respiration processes. The studied white cultivars were Chasselas (clone 14/33-4) and Petite Arvine (selection massale) grafted onto *Vitis berlandieri* × *Vitis riparia* cv. Kober 5BB rootstock. They were grown under natural field conditions with a yearly addition of foliar urea to all plants once a week for 4 weeks (4 × 5 kg N ha^{-1}; 1 ha = 10,000 m^2) during the veraison (onset of ripening marked by color change of the grape). Only the soil water status was changed. Three different irrigation regimes were established: 1) drip irrigation (DI) with a weekly feed of 9 L m^{-2} between flowering (bloom) and fruit ripening, 2) no irrigation (NI) with only rainfall as the water supply throughout the growing season, and 3) no irrigation and soil covered with a waterproof and non-reflecting plastic (NIP) to prevent the infiltration of precipitation (net-rainfall) water during the growing season (April–October).

2.2. Grapevine water status measurement

The plant water status was determined through measurement of the predawn leaf water potential (Ψ_{pd} values in megapascal, MPa) during the growing season (Zufferey et al., 2017). The Ψ_{pd} values were obtained using the pressure chamber procedure (Scholander et al., 1965; Turner, 1988) on eight single mature, undamaged, and non-senescent leaves. The measurements were done weekly, from bloom to harvest, generally from early July to September, in the morning in complete darkness between 0400 and 0500 h. The data presented here are average Ψ_{pd} values of 4 to 6 measurements during the veraison-harvest period. More negative Ψ_{pd} values indicate higher water deficit in the plant (higher pressure had to be applied to the chamber to release sap from the xylem). The plant is not stressed or low-water stressed for Ψ_{pd} values higher than −0.3 MPa; the water deficit is moderate for values between −0.3 and −0.5 MPa; and the plant is highly water-stressed for values lower than −0.5 MPa (van Leeuwen et al., 2009; Zufferey et al., 2017). Soil water potential has been reported to be very close to Ψ_{pd} (Breda et al., 1995), except when soil water conditions are not homogeneous (Améglio et al., 1999). The soil water conditions at Leytron are homogeneous, thus, we used Ψ_{pd} as a reasonable proxy for soil water potential.

2.3. Must sugars

Sugars were separated from must aliquots from Chasselas and Petite Arvine vineyards of the different irrigation treatments and 2009–2014 vintages by using ion-exchange resins in the laboratories of Agroscope. All the sugar samples were analyzed for their stable carbon isotope composition ($\delta^{13}C_{sugar}$ values) at the Institute of Earth Surface Dynamics of the University of Lausanne (IDYST-UNIL) laboratories (see below). The carbon isotope composition of the must sugars at harvest ($\delta^{13}C_{sugar}$ values) is an integral measurement of the photosynthetic fractionation during the complete vine-growing season, from bloom to harvest (Gaudillère et al., 2002). Contribution from sugar reserves from previous growing seasons cannot be excluded, although their contribution to must $\delta^{13}C_{sugar}$ values is likely to be minor.

2.4. Wine samples

The Chasselas and Petite Arvine grapes from the irrigation experiments at Leytron were harvested and vinified separately by using the same protocol at the Agroscope research winery (Changins, Switzerland). The white wines were produced by natural alcoholic fermentation of the grape-juices without the grape exocarp (skin), which contained most of the grape nitrogen content and indigenous microflora. Notably, this is the main difference between making red wine and white wine. For both wine varieties, 20 g hL^{-1} of the commercial *Saccharomyces cerevisiae* yeast culture was added to facilitate the start of fermentation. No nitrogen supplement was added for yeast nutrition. After cold stabilization at 0 °C for 1 month, the wines were bottled, evaluated for chemical and sensory properties using standard protocols, and stored at 15 °C. Bottles (n = 1 to 2) of each wine variety (Chasselas, Petite Arvine) from the 2009 to 2014 vintages and the different irrigation regimes (DI, NI and NIP) were brought to the IDYST-UNIL laboratories and stored in the dark at 4 °C until further processing.

2.5. Wine solid residues

Approximately 25 mL aliquots of each wine were transferred to 50 mL LDPE wide-necked bottles with screw caps (VWR International AG, Dietikon, Switzerland) and frozen at −20 °C for two days before

being freeze-dried on a Lyovac GT2 freeze dryer (SRK Systemtechnik GmbH, Goddelau, Germany) for 48 h. Shortly before the start of freeze-drying, the bottles were opened and the caps were replaced by preheated (480 °C, 4 h) aluminum foil, which was tightly wrapped around the bottle neck and had several holes made in the top with a clean needle. This was to avoid cross-contamination due to potential projections of wine material. Immediately after freeze-drying, the bottles containing solid residues from the dried wines (WSR) were closed with their original screw caps and stored at −20 °C until preparation for stable isotope analyses.

2.6. Stable carbon and nitrogen isotope analysis

The stable carbon and nitrogen isotope compositions were determined by elemental analysis/isotope ratio mass spectrometry (EA/IRMS), using a Carlo Erba 1108 (Fisons Instruments, Milan, Italy) elemental analyzer connected to a Delta V Plus isotope ratio mass spectrometer via a ConFlo III split interface (both of Thermo Fisher Scientific, Bremen, Germany) operated under continuous helium (He) flow (Spangenberg et al., 2006, 2017).

Flash combustion of aliquots of calibration standards and samples of berry sugars and wine solid residues was conducted at 1020 °C in a quartz reactor packed with Cr_2O_3 and $(Co_3O_4)Ag$ with a pulse of oxygen into the He carrier gas. The combustion gas products (CO_2, N_2, NO_x and H_2O) were passed through a reduction reactor at 640 °C containing elemental copper and copper oxide to reduce the non-stoichiometric nitrous products to N_2 and to remove excess oxygen from the gas stream. The gases were then dried by passing through a 10 cm long glass column filled with anhydrous $Mg(ClO_4)_2$, then passed through a gas chromatograph with a packed column (3 m × 4 mm i.d., Porapak® QS 50/80 mesh) at 70 °C for separation of N_2 and CO_2 gases, which were then analyzed for their isotopic composition on the isotope ratio mass spectrometer. Pulses of pure N_2 and CO_2 gases were injected into the He carrier flow as reference gases. Isotopic measurements and data processing were performed with ISODAT 3.0 software (Thermo Fisher Scientific). For carbon and nitrogen isotopic analyses, separate EA-combustions were done using samples aliquots of a 1:50 weight-size difference.

The stable isotope compositions were reported in the delta (δ) notation as variations of the molar ratio (R) of the heavy (^iE) to light isotope (^jE) of element E (i.e., $^{13}C/^{12}C$ and $^{15}N/^{14}N$) relative to an international standard (Coplen, 2011):

$$\delta^i E_{sample/standard} = \frac{R\left({}^iE/{}^jE\right)_{sample}}{R\left({}^iE/{}^jE\right)_{standard}} - 1$$

For carbon stable isotope ratios ($\delta^{13}C$), the standard is the Vienna Pee Dee Belemnite limestone (VPDB); for nitrogen ($\delta^{15}N$), the standard is molecular nitrogen in air (Air-N_2). The unit of the delta values is the "urey" (symbol Ur), in conformity with the International System of Units (SI) and according to the guidelines and recommendations of the International Union of Pure and Applied Chemistry (IUPAC) - Commission on Isotopic Abundances and Atomic Weights (Brand, 2011; Brand and Coplen, 2012). One milliurey (mUr) equals 1 per mil (‰), which was the unit commonly used to express the delta-value; ‰ is not an SI unit and is therefore now deprecated (Coplen, 2011).

For calibration and normalization of the measured isotopic ratios to the international scales (VPDB-LSPVEC lithium carbonate scale for $\delta^{13}C$, Air-N_2 scale for $\delta^{15}N$), a 3- or 4-point calibration was used with international reference materials (RMs) and UNIL in-house standards (Spangenberg et al., 2006; Spangenberg, 2016). The $\delta^{13}C$ and $\delta^{15}N$ values of the in-house standards were normalized with the RMs glycines ($C_2H_5NO_2$) USGS64 ($\delta^{13}C_{VPDB} = -40.81 \pm 0.04$ mUr, $\delta^{15}N_{Air\text{-}N2} = 1.76 \pm 0.06$ mUr), USGS65 ($\delta^{13}C_{VPDB} = -20.29 \pm 0.04$ mUr, $\delta^{15}N_{Air\text{-}N2} = 20.68 \pm 0.06$ mUr) and USGS66 ($\delta^{13}C_{VPDB} = -0.67 \pm 0.04$ mUr, $\delta^{15}N_{Air\text{-}N2} = 40.83 \pm 0.06$ mUr) described in Schimmelmann et al. (2016). The standards for calibration of the $\delta^{13}C$ measurements include UNIL-Glycine ($\delta^{13}C_{VPDB} = -26.02 \pm 0.05$ mUr, $\delta^{15}N_{Air\text{-}N2} = 2.93 \pm 0.09$ mUr), UNIL-Urea-1 ($\delta^{13}C_{VPDB} = -43.79 \pm 0.04$ mUr), UNIL-Pyridine ($\delta^{13}C_{VPDB} = -29.25 \pm 0.06$ mUr), and UNIL-Glucose ($\delta^{13}C_{VPDB} = -26.40 \pm 0.06$ mUr). For normalization of the $\delta^{15}N$ measurements, UNIL-Glycine, the RMs (values from Brand et al., 2014 and Schimmelmann et al., 2016) glutamic acids USGS-40 ($\delta^{15}N_{Air\text{-}N2} = -4.52 \pm 0.06$ mUr) and USGS-41 ($\delta^{15}N_{Air\text{-}N2} = 47.57 \pm 0.1$ mUr), and caffeine IAEA-600 ($\delta^{15}N_{Air\text{-}N2} = 1.02 \pm 0.05$ mUr) were used. All analyses were done at least in triplicate. The accuracy of the analyses was checked periodically through the analysis of international RMs. The repeatability and intermediate precision of the EA/IRMS analyses of must sugars and wine solid residues were determined by the standard deviation of separately replicated analyses and were better than 0.05 and 0.1 mUr for $\delta^{13}C$ and $\delta^{15}N$, respectively. The carbon and nitrogen concentrations (in wt%) were determined from the peak areas of the major isotopes using the calibrations for $\delta^{13}C_{VPDB}$ and $\delta^{15}N_{Air\text{-}N2}$. The repeatability was better than 0.2 wt% for carbon and nitrogen contents.

3. Results and discussion

3.1. Stable carbon isotope composition of must sugars

The predawn leaf water potential and the $\delta^{13}C$ values of the must sugars for Chasselas and Petite Arvine are given in Tables 1 and 2. The changes in the water deficit severity follow the different soil water treatments (DI, NI, NIP) and dryness of the vintage (summer). The lowest Ψ_{pd} values were measured in 2011 for the non-irrigated and soil plastic covered (NIP) grapevines, for both Chasselas ($\Psi_{pd} = -0.73$) and Petite Arvine ($\Psi_{pd} = -0.62$). The least water stressed grapevines were those drip irrigated (DI) during the rainy summer of 2014 ($\Psi_{pd} = -0.07$ for Chasselas, −0.08 for Petite Arvine). The measured $\delta^{13}C_{sugars}$ values (−25.33 ± 1.35 mUr) were typical for C_3 sugars from different water availability regimes during photosynthetic uptake of atmospheric CO_2. For Chasselas, the $\delta^{13}C_{sugars}$ vary from −27.29 to −22.92 mUr (−25.20 ± 1.41 mUr), and Ψ_{pd} varies between −0.07 to −0.72 MPa (−0.36 ± 0.21 MPa); for Petite Arvine, the $\delta^{13}C_{sugars}$ vary from −27.04 to −23.09 mUr (−25.46 ± 1.31 mUr), and Ψ_{pd} varies between −0.08 to −0.62 MPa (−0.32 ± 0.17 MPa). The carbon isotope composition of must sugars is highly correlated with the plant water stress severity as shown in Fig. 1A and B in the $\delta^{13}C_{sugars}$-Ψ_{pd} plots for Chasselas ($r = -0.95$, $P < 0.00001$, $n = 18$) and Petite Arvine ($r = -0.92$, $P < 0.00001$, $n = 18$). A similar good correlation between the carbon isotope composition of berry sugars and the leaf water potential was reported for field-grown vines (Gaudillère et al., 2002; de Souza et al., 2005; van Leeuwen et al., 2009). The more negative $\delta^{13}C_{sugars}$ values were measured for the less water-stressed (less negative Ψ_{pd} values) drip-irrigated vines, particularly those of the 2014, 2013 and 2012 vintages that had relatively rainy or cool summers. The higher $\delta^{13}C_{sugars}$ values were measured for the highly water-stressed vines growing on non-irrigated and plastic-covered soils during the hot and dry summers of 2009 and 2011. The must sugars from non-irrigated vines from the 2010 and 2012 vintages, characterized by cooler and relatively dry summers, had near the average $\delta^{13}C_{sugars}$ values (−25.3 mUr) and intermediate Ψ_{pd} values (−0.3 and −0.5 MPa), typical for moderately water-stressed plants. The ^{13}C-enrichment in the must sugars with different soil-water status (and induced plant water deficit) can be assessed by the isotopic fractionation between vines grown on non-irrigated and plastic-covered soils and drip-irrigated soils ($\Delta^{13}C_{NIP\text{-}DI}$) for the different vintages. The biggest differences were for Chasselas in 2013 (3.22 mUr) and for Petite Arvine in 2009 (2.62 mUr), and the lowest were for both vine varieties in 2014 (0.72 and 0.68 mUr, respectively).

Table 1
Predawn leaf water potential (Ψpd), $\delta^{13}C$ of must sugars, C and N concentrations, C/N molar ratio, and bulk $\delta^{13}C$ and $\delta^{15}N$ values of wine solid residue (WSR) from Chasselas vines grown under different soil water treatments during the 2009–2014 seasons.

Sample	Year	Soil water treatment[a]	Ψpd (MPa)[b]	$\delta^{13}C_{sugars/VPDB}$ (mUr or ‰)	TOC_{WSR} (wt%)	TN_{WSR} (wt%)	C/N_{WSR} (molar)	$\delta^{13}C_{WSR/VPDB}$ (mUr or ‰)	$\delta^{15}N_{WSR/Air-N2}$ (mUr or ‰)
CL09-280	2009	DI	−0.24 ± 0.05	−26.03 ± 0.09	30.3 ± 1.3	0.63 ± 0.04	56	−29.39 ± 0.03	2.80 ± 0.16
CL09-278	2009	NI	−0.48 ± 0.04	−23.46 ± 0.03	31.9 ± 0.9	0.49 ± 0.02	76	−27.99 ± 0.04	1.80 ± 0.11
CL09-279N	2009	NIP	−0.69 ± 0.03	−23.58 ± 0.06	31.0 ± 0.2	0.54 ± 0.00	67	−27.57 ± 0.07	1.62 ± 0.16
CL10-269	2010	DI	−0.16 ± 0.02	−26.30 ± 0.08	31.1 ± 0.5	1.36 ± 0.01	27	−29.52 ± 0.09	3.34 ± 0.19
CL10-267	2010	NI	−0.36 ± 0.05	−24.85 ± 0.03	32.1 ± 0.4	1.10 ± 0.00	34	−29.31 ± 0.18	2.95 ± 0.15
CL10-268	2010	NIP	−0.53 ± 0.03	−24.70 ± 0.18	31.7 ± 0.2	0.78 ± 0.01	47	−28.46 ± 0.09	2.24 ± 0.02
CL11-285	2011	DI	−0.27 ± 0.03	−25.45 ± 0.01	31.1 ± 1.9	0.87 ± 0.01	42	−29.13 ± 0.21	3.06 ± 0.07
CL11-283	2011	NI	−0.50 ± 0.04	−24.54 ± 0.04	34.0 ± 1.4	0.63 ± 0.00	63	−28.25 ± 0.07	1.94 ± 0.12
CL11-284	2011	NIP	−0.73 ± 0.04	−22.92 ± 0.04	31.8 ± 0.5	0.52 ± 0.01	71	−26.96 ± 0.02	1.13 ± 0.17
CL12-278	2012	DI	−0.15 ± 0.03	−26.51 ± 0.04	32.8 ± 0.6	0.90 ± 0.06	42	−28.60 ± 0.07	2.44 ± 0.02
CL12-276	2012	NI	−0.41 ± 0.04	−25.28 ± 0.06	32.6 ± 0.2	0.94 ± 0.01	40	−28.45 ± 0.03	3.74 ± 0.06
CL12-277	2012	NIP	−0.60 ± 0.03	−23.50 ± 0.02	31.1 ± 0.9	0.75 ± 0.01	48	−27.55 ± 0.05	2.22 ± 0.09
CL13-270	2013	DI	−0.13 ± 0.03	−26.39 ± 0.12	32.6 ± 1.6	0.86 ± 0.01	44	−29.64 ± 0.13	2.92 ± 0.10
CL13-268	2013	NI	−0.28 ± 0.03	−26.32 ± 0.08	33.0 ± 0.9	0.73 ± 0.01	53	−29.72 ± 0.06	2.53 ± 0.15
CL13-269	2013	NIP	−0.58 ± 0.03	−23.17 ± 0.03	32.1 ± 0.6	0.59 ± 0.01	63	−27.64 ± 0.03	1.76 ± 0.12
CL14-306	2014	DI	−0.07 ± 0.02	−27.26 ± 0.11	33.4 ± 0.4	1.39 ± 0.08	28	−29.26 ± 0.15	2.94 ± 0.07
CL14-304	2014	NI	−0.10 ± 0.02	−26.83 ± 0.07	32.3 ± 1.0	1.41 ± 0.01	27	−29.36 ± 0.11	2.98 ± 0.08
CL14-305	2014	NIP	−0.27 ± 0.03	−26.54 ± 0.13	31.4 ± 0.7	0.94 ± 0.02	38	−29.18 ± 0.02	2.85 ± 0.09

[a] DI = drip irrigation (9 L water m^{-2} per week between flowering and veraison), NI = no irrigation, NIP = no irrigation and plastic-covered soil.
[b] Average Ψ_{pd} values of 4 to 6 measurements during the veraison-harvest period ± one standard deviation.

3.2. Carbon isotope composition of wine solid residues

The residual colloidal gel solids obtained by freeze-frying aliquots of Chasselas and Petite Arvine wines had 30.1 to 34.0 wt% (32.0 ± 1.0 wt%) total organic carbon (TOC_{WSR}) and carbon isotope ratios ($\delta^{13}C_{WSR}$ values) between −29.72 to −26.21 mUr (−28.17 ± 0.94 mUr) (Tables 1 and 2). The carbon isotope fractionation between wine solid residues and must sugars ($\Delta^{13}C_{WSR\text{-}sugars}$) varied between −4.53 and −1.01 mUr, in agreement with the origin of most wine organic compounds from alcoholic fermentation of vine berry sugars. The loss during freeze-drying of the relatively ^{13}C-enriched main fermentation products, carbon dioxide and ethanol, explains the lower $\delta^{13}C$ values of the wine solid residues compared to the must sugars from the same cultivar (Figs. 1 and 2). Therefore, the $\delta^{13}C_{WSR}$ values are significantly correlated with the Ψ_{pd} values as observed for the must sugars (Fig. 1C,D). The ^{13}C-enrichment measured in the solid residues of wines derived from NIP compared to DI vines shows the same trend observed for must sugars but are between 0.6 and 1 mUr smaller. Specifically, the vintages showing the biggest differences in Chasselas wines were 2011 and 2013 (2.17 and 2.00 mUr, respectively), and those in Petite Arvine were 2009 and 2011 (both 1.73 mUr); the smallest differences for Chasselas and Petite Arvine were in 2014 wines (for both, the same value of 0.08 mUr). Similar trends were observed for the Pinot Noir red wines obtained from similar irrigation experiments (DI, NI, NIP) and 2009–2014 vintages (Spangenberg et al., 2017). The highly significant correlation between the $\delta^{13}C$ values of the must sugars and the vine water deficit severity observed for all vine cultivars (Chasselas, Petite Arvine, and Pinot noir; $r = -0.94$, $P < 0.00001$, $n = 54$) is well preserved in the wine solid residues, showing $\delta^{13}C_{WSR}$-Ψ_{pd} correlation values of −0.70 ($P < 0.00001$, $n = 54$) (Fig. 3A,B). The statistical $\delta^{13}C_{WSR}$-Ψ_{pd} relationships are essentially the same for the three varieties ($r = -0.89$ for Chasselas, $r = -0.88$ for Petite Arvine, Fig. 1C,D, and $r = -0.89$ for Pinot noir, Fig. 1B in Spangenberg et al., 2017, all with $P < 0.00001$). They define similar regression lines in the $\delta^{13}C_{WSR}$-Ψ_{pd} plot (Fig. 3B) with the same slope (−3.59 and −3.61) and intercept (−30.00 and −30.01) for Chasselas

Table 2
Predawn leaf water potential (Ψpd), $\delta^{13}C$ of must sugars, C and N concentrations, C/N molar ratio, and bulk $\delta^{13}C$ and $\delta^{15}N$ values of wine solid residue (WSR) from Petite Arvine vines grown under different soil water treatments during the 2009–2014 seasons.

Sample	Year	Soil water treatment[a]	Ψpd (MPa)[b]	$\delta^{13}C_{sugars/VPDB}$ (mUr or ‰)	TOC_{WSR} (wt%)	TN_{WSR} (wt%)	C/N_{WSR} (molar)	$\delta^{13}C_{WSR/VPDB}$ (mUr or ‰)	$\delta^{15}N_{WSR/Air-N2}$ (mUr or ‰)
AR09-269	2009	DI	−0.22 ± 0.05	−26.12 ± 0.24	31.1 ± 0.1	0.74 ± 0.01	49	−27.94 ± 0.03	2.36 ± 0.11
AR09-267	2009	NI	−0.39 ± 0.04	−24.49 ± 0.07	32.6 ± 1.1	0.66 ± 0.02	57	−27.10 ± 0.18	2.91 ± 0.08
AR09-268	2009	NIP	−0.59 ± 0.04	−23.50 ± 0.02	32.1 ± 0.2	0.62 ± 0.01	60	−26.21 ± 0.06	2.37 ± 0.14
AR10-257	2010	DI	−0.15 ± 0.02	−26.81 ± 0.01	30.5 ± 0.8	0.80 ± 0.01	44	−28.63 ± 0.01	3.06 ± 0.04
AR10-255	2010	NI	−0.32 ± 0.05	−25.85 ± 0.01	32.8 ± 0.6	0.96 ± 0.01	40	−27.74 ± 0.10	2.58 ± 0.12
AR10-256	2010	NIP	−0.45 ± 0.04	−24.60 ± 0.09	33.7 ± 0.7	1.23 ± 0.04	32	−27.02 ± 0.01	2.49 ± 0.20
AR11-273	2011	DI	−0.22 ± 0.03	−25.23 ± 0.08	32.7 ± 0.5	0.96 ± 0.02	40	−28.19 ± 0.15	4.00 ± 0.34
AR11-271	2011	NI	−0.46 ± 0.03	−24.16 ± 0.22	33.3 ± 0.8	0.94 ± 0.01	41	−27.12 ± 0.17	3.30 ± 0.15
AR11-272	2011	NIP	−0.62 ± 0.04	−23.09 ± 0.03	33.5 ± 1.4	0.72 ± 0.01	54	−26.46 ± 0.21	2.90 ± 0.11
AR12-266	2012	DI	−0.17 ± 0.02	−26.91 ± 0.03	30.1 ± 0.1	0.68 ± 0.01	52	−28.73 ± 0.12	2.51 ± 0.01
AR12-264	2012	NI	−0.45 ± 0.04	−25.14 ± 0.23	32.4 ± 1.3	0.65 ± 0.04	58	−27.74 ± 0.13	2.29 ± 0.04
AR12-265	2012	NIP	−0.57 ± 0.04	−24.51 ± 0.18	30.6 ± 0.6	0.76 ± 0.00	47	−27.23 ± 0.09	2.75 ± 0.12
AR13-267	2013	DI	−0.12 ± 0.02	−26.62 ± 0.16	32.1 ± 0.9	0.53 ± 0.01	70	−28.37 ± 0.13	3.08 ± 0.33
AR13-265	2013	NI	−0.23 ± 0.04	−26.84 ± 0.11	30.1 ± 0.7	0.46 ± 0.00	77	−28.46 ± 0.05	1.59 ± 0.11
AR13-266	2013	NIP	−0.39 ± 0.03	−24.04 ± 0.07	31.9 ± 0.6	0.66 ± 0.01	56	−26.85 ± 0.08	0.99 ± 0.16
AR14-303	2014	DI	−0.08 ± 0.02	−27.04 ± 0.01	32.5 ± 0.8	1.10 ± 0.01	35	−28.05 ± 0.05	3.33 ± 0.06
AR14-301	2014	NI	−0.12 ± 0.02	−26.98 ± 0.02	32.5 ± 0.5	0.83 ± 0.02	46	−28.18 ± 0.03	2.65 ± 0.10
AR14-302	2014	NIP	−0.24 ± 0.03	−26.36 ± 0.13	33.0 ± 0.1	0.61 ± 0.01	63	−27.97 ± 0.05	2.62 ± 0.03

[a] DI = drip irrigation (9 L water m^{-2} per week between flowering and veraison), NI = no irrigation, NIP = no irrigation and plastic-covered soil.
[b] Average Ψ_{pd} values of 4 to 6 measurements during the veraison-harvest period ± one standard deviation.

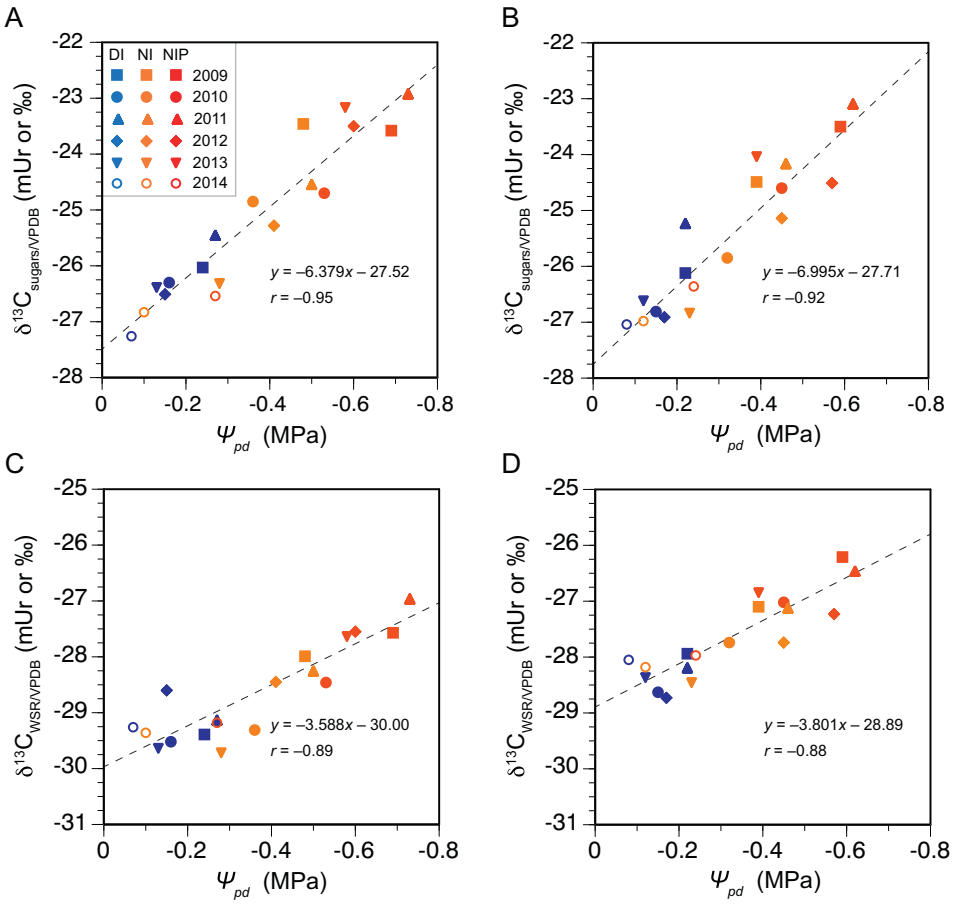

Fig. 1. Carbon isotope composition of must sugars ($\delta^{13}C_{sugars}$) and wine solid residue ($\delta^{13}C_{WSR}$) versus predawn leaf water potential (Ψ_{pd}) of Chasselas (A, C) and Petite Arvine (B, D) vines grown under different soil water treatments (DI = drip irrigation, NI = no irrigation, NIP = no irrigation and plastic- covered soil) during growing seasons 2009–2014.

and Pinot noir but similar slope and different intercept for Petite Arvine ($\delta^{13}C_{WSR} = -3.80\Psi_{pd} - 28.89$). These results suggest that the correlation between the $\delta^{13}C$ values of wine solid residues and the severity of vine water deficit may be general and valid for all varieties. The $\delta^{13}C_{WSR}$ values for Petite Arvine are systematically 1.1 mUr enriched compared to those for Chasselas and Pinot noir (Fig. 3B). This difference is explained by the characteristic and relatively very high content of organic volatiles (aroma and flavor compounds) in Arvine wines (Fretz et al., 2005a), which are ^{13}C-depleted compared to the less- and non-volatile compounds, and preferentially loss during freeze-drying. Now, we can confirm that the $\delta^{13}C_{WSR}$-Ψ_{pd} relationship is valid for white wine (e.g., Chasselas and Petite Arvine, this study) and red wines (e.g., Pinot noir, Spangenberg et al., 2017) and does not depend on the application of fertilizers (i.e., foliar urea to Chasselas and Petite Arvine vines, nothing to Pinot noir), nor on the absence or presence of the grape's skin during juice fermentation for making a white or red wine, respectively. Thus, the carbon isotope composition of the solid residues of wines records the plant water status (i.e., the severity of plant water deficit) and as such the water availability in the vineyard soils. The difference in the intercept of the $\delta^{13}C_{WSR}$-$\delta^{13}C_{sugar}$ regression equation for

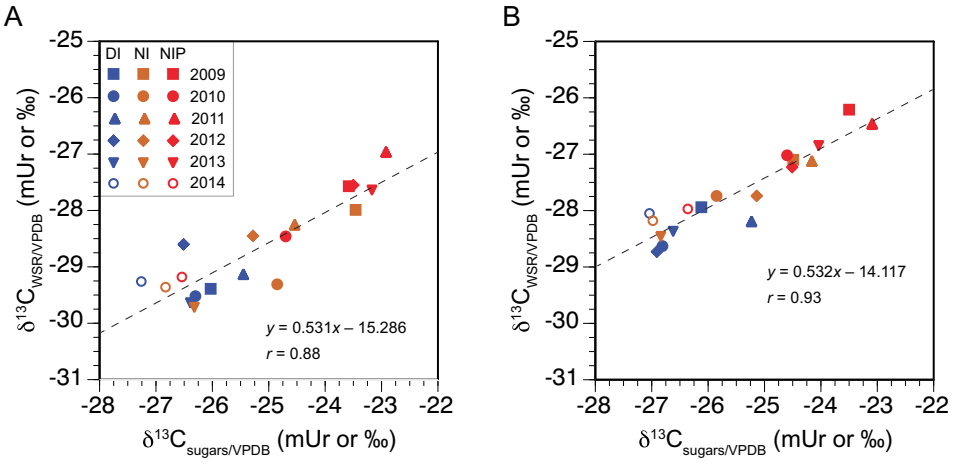

Fig. 2. Carbon isotope compositions of wine solid residue ($\delta^{13}C_{WSR}$) versus must sugars ($\delta^{13}C_{sugars}$) of Chasselas (A) and Petite Arvine (B) vines grown under different soil water treatments during the 2009–2014 seasons. Same symbols and color coding as in Fig. 1.

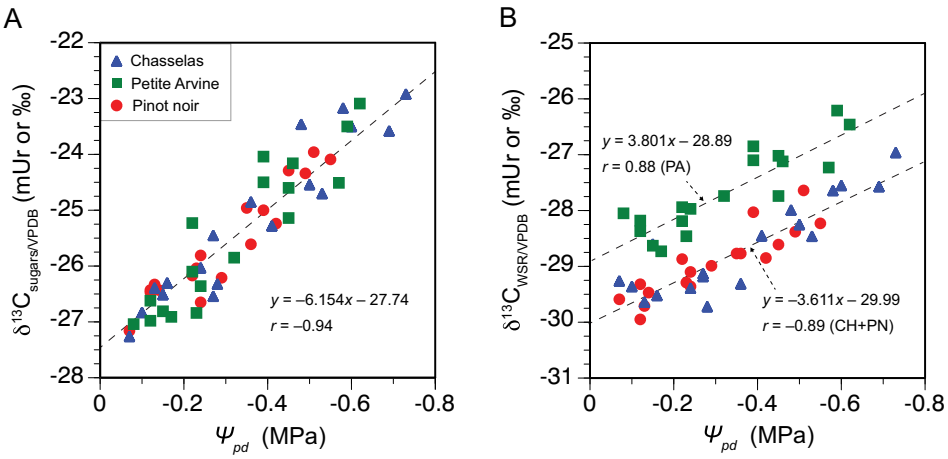

Fig. 3. Comparison of the $\delta^{13}C_{sugars}$-Ψ_{pd} (A) and $\delta^{13}C_{WSR}$-Ψ_{pd} (B) relationships for Chasselas, Perite Arvine and Pinot noir vines grown under different soil water treatments during the 2009–2014 seasons.

Petite Arvine compared to that for Chasselas and Pinot noir is similar in direction and magnitude (+1 mUr) to the $\delta^{13}C$ differences in the $\delta^{13}C_{WSR}$-Ψ_{pd} plot (Figs. 3B and 4A). This confirms that these differences are due to distinct carbon metabolism in Petite Arvine compared to Chasselas and Pinot noir (explained below). These results suggest that a variety-specific response of $\delta^{13}C_{WSR}$ to water deficit (i.e., extent of the $\delta^{13}C_{WSR}$-Ψ_{pd} correlation) can be excluded.

3.3. C/N ratios and stable nitrogen isotope ratios of wine solid residues

Discrimination against ^{15}N during the processes of (soil or foliar) N uptake, assimilation, translocation, and partitioning explain the differences in the $\delta^{15}N$ values of plant tissues/organs (Choi et al., 2005; Evans, 2001; Robinson, 2001; Verdenal et al., 2015). The total nitrogen content in the wine solid residues (TN_{WSR} values) and its nitrogen stable isotope ratios ($\delta^{15}N_{WSR}$) are dependent on the sources of nitrogen compounds and their relative contribution in grapes, originating from indigenous organic compounds (e.g., free amino acids, peptides, proteins, pyrazines, pyridines) mainly in the skin (exocarp) and pulp (mesocarp) cells from berries, potential residual nitrogen from foliar N fertilizer (e.g., urea), and potential yeast culture starter and N nutrients (e.g., ammonium salts or vitamins) added to enhance yeast metabolism and stimulate yeast growth during winemaking. The TN_{WSR} values for all wines varied from 0.46 to 1.41 wt%; no significant difference was observed between the Chasselas (0.86 ± 0.29 wt%) and Petite Arvine (0.77 ± 0.20 wt%) wines (Tables 1 and 2). The C/N ratios for the Chasselas and Petite Arvine wine solid residues are relatively lower (higher TN) than those for Pinot noir, reflecting that nitrogen fertilization was applied to the white wine cultivars, and none to Pinot noir vines (Fig. 4B). The Chasselas and Pinot noir wines define regression lines in the C/N_{WSR}-$\delta^{15}N_{WSR}$ plot with similar slope, different from that for Petite Arvine (Fig. 4B). Also, the white wine varieties (Chasselas, Petite Arvine) record a dissimilar response of the vine to nitrogen and soil water availability. In Chasselas wines the TN decreased and the C/N molar ratio increased with increasing plant water stress severity (Table 1, Fig. 5A); specifically, the C/N ratios were highly correlated with the Ψ_{pd} values ($r = 0.75$, $P = 0.00032$). This clearly follows the soil water status/availability set by the different irrigation treatments, with TN decreasing and C/N increasing in the order NIP < NI < DI. Such a trend was not observed in the Petite Arvine wines ($r = -0.01$, Table 2, Fig. 5B).

In contrast to the carbon isotope ratios, the nitrogen isotope ratios of the solid residues from Chasselas wines decreased with increasing plant water stress, i.e., lower Ψ_{pd} values (Fig. 5C). The $\delta^{15}N_{WSR}$-Ψ_{pd} correlation is highly significant ($r = 0.75$, $P = 0.00033$). ^{15}N-depletion estimated by the difference between the $\delta^{15}N_{WSR}$ values from NIP and DI irrigation treatments ($\Delta^{15}N_{NIP\text{-}DI}$) was higher for the wines from dry summer vintages. The largest $\Delta^{15}N_{NIP\text{-}DI}$ value was −1.93 for 2011 wines, and values were between −1.18 and −1.10 mUr for 2009, 2010 and 2013. For the vintages with a rainy summer, as those of 2012 and 2014, the $\delta^{15}N_{WSR}$ difference between NIP and DI was small (−0.22 and −0.10 mUr, respectively). These C/N_{WSR} and $\delta^{15}N_{WSR}$ trends versus water stress severity were similar to those described for the first time in Pinot noir red

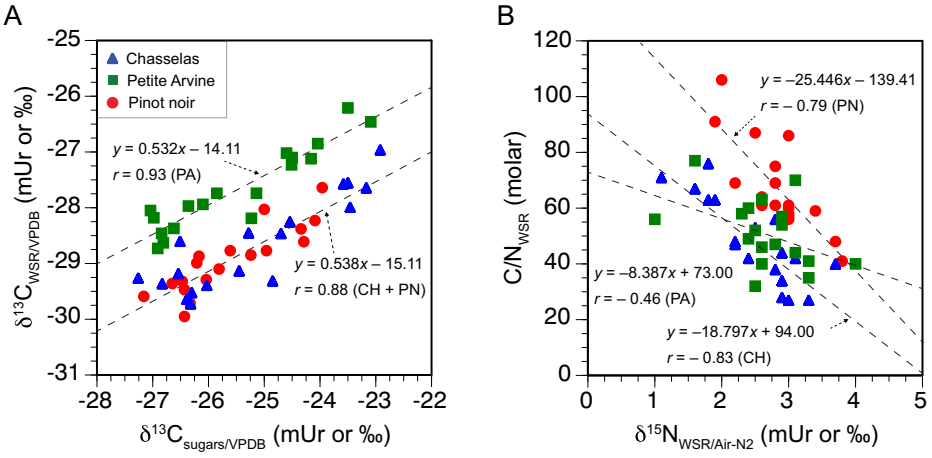

Fig. 4. Comparison of the $\delta^{13}C_{WSR}$-$\delta^{13}C_{sugars}$ (A) and C/N molar ratios (C/N_{WSR}) versus nitrogen isotope composition of wine solid residue ($\delta^{15}N_{WSR}$) (B) relationships for Chasselas, Perite Arvine and Pinot noir vines grown under different soil water treatments during the 2009–2014 seasons.

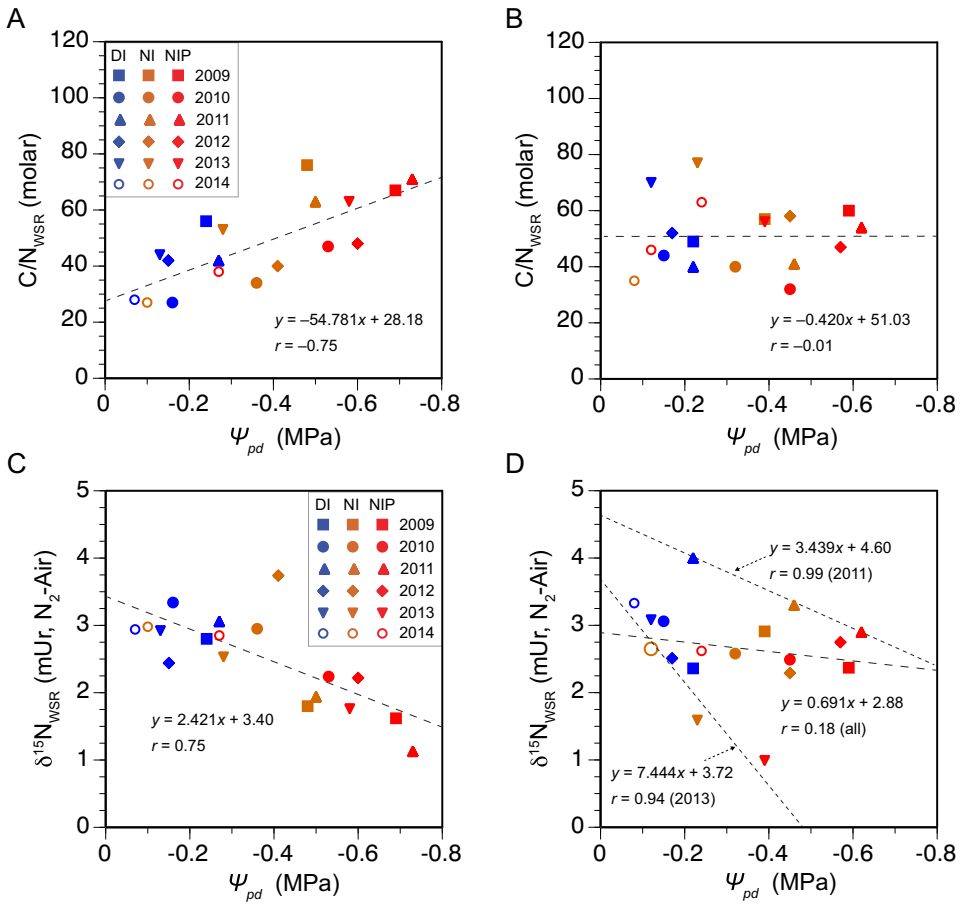

Fig. 5. C/N_{WSR} and $\delta^{15}N_{WSR}$ versus Ψ_{pd} of Chasselas (A, C) and Petite Arvine (B, D) vines grown under different soil water treatments during the 2009–2014 seasons. Same symbols and color coding as in Fig. 1.

wines from the Agroscope experimental station at Leytron (Spangenberg et al., 2017). These trends can be understood because the soil water status (supplied soil water) controls the root uptake of water and water-soluble nutrients. In dried soils, nitrogen in the form of nitrate or ammonium is less available to the plants (Ellsworth and Sternberg, 2016). Nutrients such as nitrogen are translocated through the xylem with the transpiration stream. In dried soils, transpiration flow to the canopy decreases, and consequently, N uptake and transport also decrease. The nitrogen content in the plant organs (e.g., grape) will decrease and will depend mostly on the remobilization of N- nutrient reserves in roots (e.g., Millard and Neilsen, 1989; Bates et al., 2002). The major forms of the remobilized organic nitrogen are proteins and their breakdown products, which are depleted in ^{15}N compared to the soil nitrogen species. Therefore, grape must and derived wine solid residues from water stressed vines will have lower TN_{WSR} contents and lower $\delta^{15}N_{WSR}$ values than drip-irrigated vines. This is clearly shown in this study for the white wine Chasselas (Fig. 4), confirming the trends reported for the red wine Pinot noir (Spangenberg et al., 2017). However, for Petite Arvine, no clear relationship was found between C/N_{WSR} or $\delta^{15}N_{WSR}$ and plant water status (Fig. 5B,D). Only for the 2011 and 2013 vintages—as for Chasselas and Pinot noir—was an increase $\delta^{15}N$ values observed, in the order NIP < NI < DI (Fig. 5D). It is important to note that the highly significant correlations of C/N-$\delta^{15}N$ and $\delta^{13}C$-$\delta^{15}N$ in Chasselas wine solid residues (Fig. 6A,C) serve as indicators of soil water availability in a vineyard, as has been demonstrated to a similar extent for the field-measured Ψ_{pd} data and the $\delta^{13}C$ in must sugars. Again, such correlations were not found for Petite Arvine (Fig. 6B,D). We looked for an explanation for this different behavior of N in Petite Arvine wines. On average the yeast assimilable nitrogen (YAN) in Petite Arvine must from the different irrigation regimes and the 2009–2014 vintages were statistically significant higher than in Chasselas and Pinot noir (Zufferey et al., *unpublished data*). Same nitrogen fertilization levels, in amount and timing, were applied to the Chasselas and Petite Arvine vines; no fertilization was applied to the Pinot noir vines (Zufferey et al., 2017). The three grapevine varieties were grafted onto the same rootstock (*Vitis berlandieri* x *Vitis riparia* cv. Kober 5BB); consequently there were no differences in the processes of N uptake and/or assimilation by N-fixing bacteria in the rhizosphere of the three varieties. Thus, the dissimilar effects of irrigation on the nitrogen metabolism (assimilation, translocation, accumulation) in Petite Arvine compared to Chasselas and Pinot noir grapevines was due to genetic differences in N uptake and N-use efficiency. Petite Arvine is considered a genetic curiosity, it is among the 12% of 2344 studied *Vitis vinifera* L. cultivars which are unrelated to other grape varieties (Lacombe et al., 2013). The variability of crop plant genotypes and nitrogen use efficiency (NUE) is well document for C_3 and C_4 metabolisms, more specifically for wheat (Cormier et al., 2016), rice (Rakotoson et al., 2017), rapeseed (Bouchet et al., 2016), maize (Ge et al., 2018), and sugarcane (Robinson et al., 2007), but no studies showing NUE variability in grapevine genotypes were published. Different utilization (metabolism) of nitrogen in Petite Arvine compared to Chasselas and Pinot noir may be due to genetic differences. Further research is required to identify and understand the genetic basis (molecular mechanisms and individual genes) of these N metabolism traits.

A good correlation of $\delta^{13}C$ and water soil availability is preserved in wine solid residues from all studied grape varieties (Chasselas, Petite Arvine, Pinot noir). The nitrogen isotope composition of dried wines may be used in most cases—except Petite Arvine—to confirm the information on the plant water status provided by the $\delta^{13}C$ values; this is valid even when nitrogen was partially provided by fertilization.

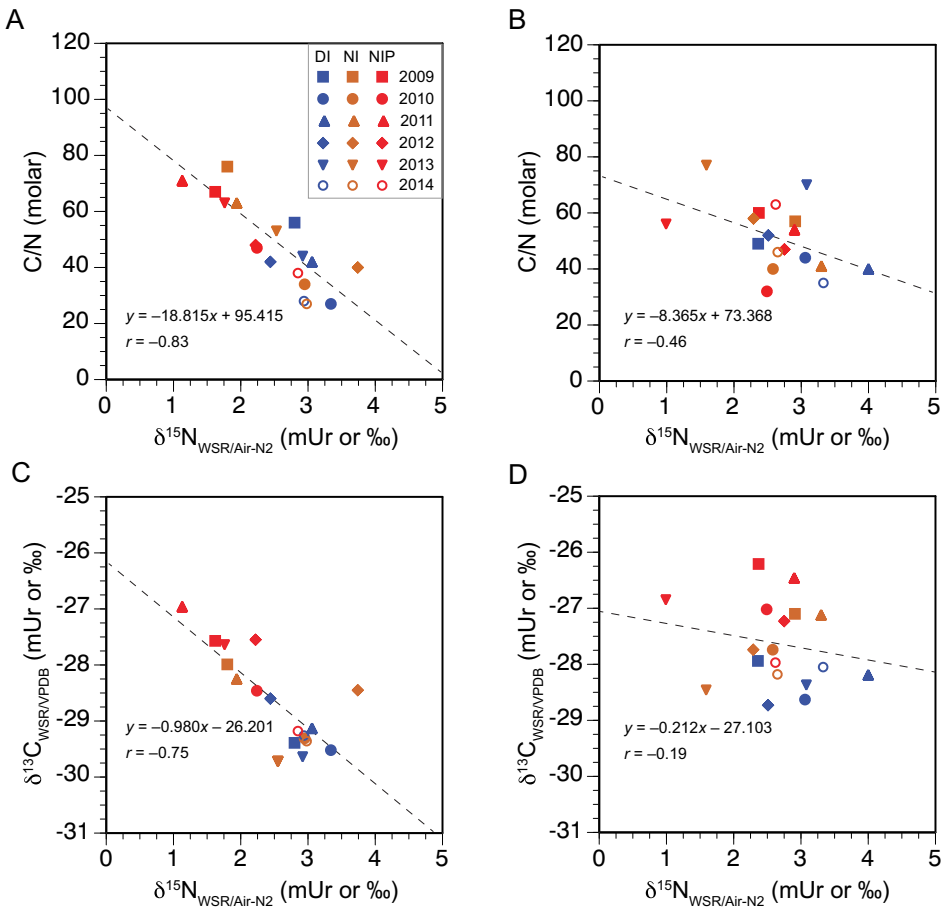

Fig. 6. C/N_{WSR} and $\delta^{13}C_{WSR}$ versus $\delta^{15}N_{WSR}$ of Chasselas (A, C) and Petite Arvine (B, D) vines grown under different soil water treatments during the 2009–2014 seasons. Same symbols and color coding as in Fig. 1.

Furthermore, our results show that the C/N and $\delta^{15}N$ values of wine solid residues serve as indicators of the nitrogen supply to the plant-fruit and N dynamics in the soil-water-plant system.

4. Conclusion

The carbon isotope composition of solid residues obtained by freeze-drying aliquots of wine is highly correlated with the soil water availability controlled by different irrigation regimes, the field-measured plant water status and the dryness of the vintage summer. The variations in these $\delta^{13}C_{WSR}$ values mimic those of the carbon isotope composition of sugars in grapevine (must sugars), which is a well-established and widely used indicator of grapevine water status. The $\delta^{13}C_{WSR}$ is a new indicator of soil water availability in vineyard regions, and its evolution can be traced back several decades from the present day; thus, it can be used as an integral sensor for monitoring the impact of global warming and local climate variability during successive growing seasons in viticultural regions. Similar approaches may be applicable to other water-soil-plant systems and crop-derived products. Finally, the C/N and $\delta^{15}N_{WSR}$ values serve as indicators of the nitrogen supply to the plant-fruit and of N dynamics in water-soil-plant systems.

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